

## **Cost-Effective Surface Modification for Metallic Bipolar Plates**

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### **Objectives**

- Develop a low cost metallic bipolar plate alloy that will form an electrically conductive and corrosion resistant nitride surface layer during thermal nitriding to enable use in a proton exchange membrane (PEM) fuel cell environment.

### **Technical Barriers**

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost.
- P. Durability

### **Approach**

- Conduct a study of the nitridation behavior of a series of model Ni/Fe-X base alloys (X = nitride forming elements such as Cr, Nb, Ti, V) that can potentially meet DOE bipolar plate cost goals.
- Identify the most promising combination of X additions, ternary and higher order alloying elements, and nitriding conditions that result in the formation of an adherent, protective nitride surface layer.
- Evaluate the corrosion, electrical properties, and fuel cell behavior of the thermally nitrided alloys.
- Characterize the nitride layer microstructure and composition by x-ray diffraction, electron probe microanalysis, scanning electron microscopy, and transmission electron microscopy. Use this information in a feedback loop to modify alloy chemistry and nitridation processing conditions to optimize the protectiveness of the nitride surface layer.

### **Accomplishments**

- Nitridation of a model Ni-50Cr alloy was optimized to form a dense, protective CrN/Cr<sub>2</sub>N surface layer.
- The nitrided model Ni-50Cr alloy exhibited very low levels of metal-ion dissolution and negligible increase in contact resistance in a 1000-hour single-cell, fuel cell test using 50 cm<sup>2</sup> active area anode and cathode plates and in a 4100-hour bipolar coupon corrosion test.

- A United States patent disclosure was submitted in April 2003 for nitrided Ni/Fe-Cr and related base alloys thermally nitrided to form a protective CrN/Cr<sub>2</sub>N surface layer.
- Collaboration was established with DANA Corporation, Tennessee Technological University, and the University of Minnesota to evaluate sealing and manufacturability issues of nitrided Ni-Cr alloys and to demonstrate technological viability of the approach by a 5-cell stack test.

### **Future Directions**

- Continue in-cell evaluation of nitrided Ni-50Cr to fully characterize and optimize the protectiveness of the CrN/Cr<sub>2</sub>N surface layer. This testing will include single-cell and stack testing with Los Alamos National Laboratory (LANL) and fuel cell manufacturers.
- Modify alloy composition/nitriding conditions to form a corrosion-resistant CrN/Cr<sub>2</sub>N surface layer on Ni/Fe-Cr base alloys that are comparable to conventional stainless steels in terms of manufacturability and cost in order to meet DOE bipolar plate cost goals. Establish partnerships with alloy producers and fuel cell manufacturers.

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### **Introduction**

The bipolar plate is one of the most expensive components in PEM fuel cells. Thin metallic bipolar plates offer the potential for significantly lower cost than currently-used machined graphite bipolar plates and reduced weight/volume and better performance than developmental polymer/ carbon fiber and graphite composite bipolar plates. However, inadequate corrosion resistance can lead to high electrical resistance and/or contamination of the polymer membrane, both of which can significantly degrade performance. Metal nitrides offer electrical conductivities up to an order of magnitude greater than that of graphite and are highly corrosion resistant. Unfortunately, most conventional coating methods (for metal nitrides) are too expensive for PEM fuel cell stack commercialization or tend to leave pin-hole defects, which result in accelerated local corrosion and unacceptable performance.

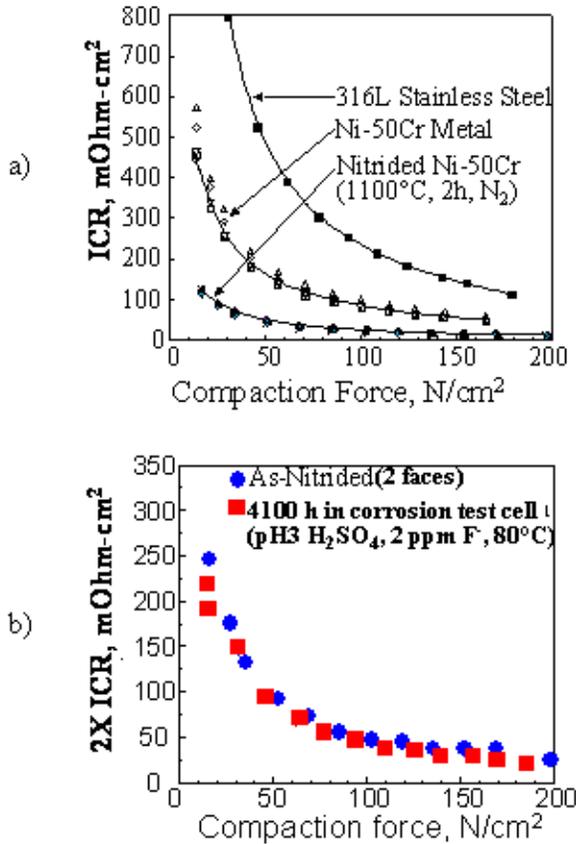
### **Approach**

The goal of this effort is to develop a bipolar plate alloy that will form an electrically conductive and corrosion resistant nitride surface layer during thermal (gas) nitriding. There are three advantages to this approach. First, because the nitriding is performed at elevated temperatures, pin-hole defects are not expected because thermodynamic and kinetic factors favor complete conversion of the metal surface to nitride. Rather, the key issues are nitride

layer cracking, adherence, and morphology (discrete internal subsurface precipitates vs. continuous external scales), which can potentially be controlled through proper selection of alloy composition and nitridation conditions. Second, the alloy can be formed into final shape by inexpensive metal forming techniques such as stamping prior to thermal nitridation. Third, thermal nitridation is an inexpensive, well-established industrial technique.

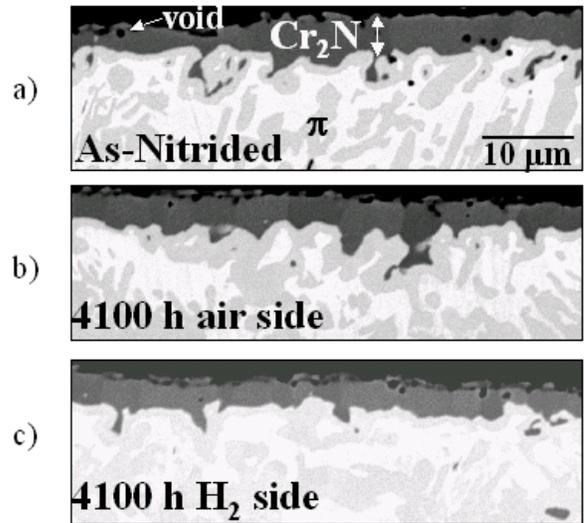
### **Results**

A nitrided Ni-50Cr model alloy coupon was exposed for 4100 hours (h) under simulated PEM fuel cell anode and cathode bipolar plate conditions using the corrosion test cell developed at LANL [1]. The test environment was a pH 3 solution of H<sub>2</sub>SO<sub>4</sub> containing 2 ppm F<sup>-</sup> at 80°C. Hydrogen and air at 1 atmosphere were supplied to the anode and cathode faces, respectively, of the flat (no flow field features) test coupon. Platinum screens passed 1 A/cm<sup>2</sup> electrical current to the ELAT® electrode/carbon backing paper/bipolar test coupon assembly, and the electrical potential was recorded in-situ to monitor resistive surface phase (e.g. oxide) growth. In the corrosion test cell, the nitrided Ni-50Cr bipolar coupon exhibited a voltage change of only 2 mV/1000 h at the anode and 2.7 mV/1000 h at the cathode over the course of the 4100 h exposure. The anode face of the coupon effectively experienced ~ -0.31 V vs standard hydrogen electrode (SHE) and the cathode face +0.56 V. Ni levels of only 0.85,



**Figure 1.** Interfacial contact resistance data a) as-nitrided b) after 4100 h in corrosion test cell. Note that the data for the bipolar coupon from the corrosion test cell include both anode and cathode faces; the as-nitrided comparative data from Figure 1a was therefore doubled.

0.56, and 2.4 ppm were measured in the anode-face exposed solutions and 0.034, 0.019, and 0.027 ppm Ni in the cathode-face exposed solutions, respectively, for 0-1500, 1500-3400, and 3400-4100 hours of exposure. Cr was not detected. Interfacial contact resistance (ICR) data as a function of compaction pressure are shown in Figure 1. The Ni-50Cr alloy (no nitridation treatment) had a lower contact resistance than 316L stainless steel, shown for comparative purposes. Subsequent nitridation of Ni-50Cr significantly lowered contact resistance (Figure 1a). ICR measurements of the 4100 h exposed bipolar test coupon (Figure 1b) showed no increase in ICR relative to as-nitrided Ni-50Cr. Back scattered electron (BSE) images of a nitrided Ni-50Cr control coupon, the 4100 h cathode-environment exposed face, and the 4100 h anode-



**Figure 2.** Back Scattered Electron Cross-Sections of Nitrided Ni-50Cr a) as-Nitrided b) 4100 h Air (cathode face) Exposure in Corrosion Test Cell, c) 4100 h H<sub>2</sub> (anode face) Exposure in Corrosion Test Cell

environment exposed face, are shown in Figure 2. The external nitride scale consisted of three layers: a ~1 micron thick semi-continuous outer layer of CrN (not visible in the figure); an intermediate, 3-5 microns thick continuous layer of Cr<sub>2</sub>N; and an inner layer of the ternary Ni-Cr-N π phase. The microstructure of the nitride on the cathode-exposed face (Figure 2b) and the anode-exposed face (Figure 2c) appeared essentially the same as the archival, as-nitrided material, with no evidence of significant attack or surface oxide formation (based on transmission electron microscopy cross-sections).

A single-cell fuel cell test was subsequently conducted using 50 cm<sup>2</sup> active area anode and cathode plates of nitrided Ni-50Cr with a simple serpentine flow-field groove pattern (Figure 3). The membrane electrode assembly (MEA) was Nafion<sup>®</sup> 112 with anode and cathode loadings of ~ 0.20 mg Pt/cm<sup>2</sup>. The gas diffusion layers (backings) were uncatalyzed ELAT<sup>®</sup>. Double-sided ELAT<sup>®</sup> was used on the anode sides and single-sided on the cathodes. The cells were operated at 3 atmospheres (absolute) and at 80°C. Purified hydrogen was introduced to the cell at 0.3 standard liters per minute (SLPM) and compressed room air at 1.8 SLPM. The fuel cell was operated continuously at 0.7 V



**Figure 3.** Nitrided Ni-50Cr Cathode Plate from Single-Cell Fuel Cell Test

An inadvertent cutoff in the supply of hydrogen to the cell during the test resulted in membrane damage and performance degradation such that the test was halted after 500 h, and the damaged MEA was replaced. A second MEA was prepared with anode/cathode loadings of 0.23/0.37 mg Pt/cm<sup>2</sup> on a thicker membrane, Nafion<sup>®</sup> 1135. It was operated for 500 h, for a total of ~1,000 h of in-cell testing of the nitrided plates. Cell resistance, an indicator of membrane contamination, did not increase a discernable amount over the second 500 h (resistances were measured with the initial MEA but were untrustworthy due to the damaged MEA). The baseline interfacial resistance contributions between the nitrided plates and the adjacent gold-coated current collector plates were 5 mΩ-cm<sup>2</sup> at the cathode plate and 1 mΩ-cm<sup>2</sup> at the anode (the total-cell resistances were on the order of 130 mΩ-cm<sup>2</sup>).

X-ray fluorescence indicated only trace levels of Ni and Cr in the MEAs after the single-cell fuel cell test, in the range of only 0.01 to 0.3 x 10<sup>-6</sup> g/cm<sup>2</sup>. This level of contamination is extremely low and consistent with the stable, inert, and protective behavior of the CrN/Cr<sub>2</sub>N surface. Some stagnant liquid was observed in one of the alignment pin ports on disassembly of the cell and was subsequently found to be Cr-rich. However, little Cr or other contamination was observed in the membrane in the area surrounding this alignment pin. A local casting flaw and/or compositional inhomogeneity (e.g., inclusion) in the alloy is suspected to have led to

poor nitridation at this spot, making it vulnerable to attack.

### **Conclusions**

The results of the 4100 h corrosion test and the 1000 h single-cell fuel cell test demonstrate the potential of thermally grown CrN/Cr<sub>2</sub>N surface layers on Cr-bearing alloys to:

- 1 prevent significant metal-ion membrane contamination,
- 2 maintain low contact resistance, and
- 3 effectively cover and protect flow-field groove features under PEM fuel cell bipolar plate operating conditions.

Future work will focus on the formation of corrosion-resistant CrN/Cr<sub>2</sub>N surface layers on Ni/Fe-Cr base alloys that are comparable to conventional stainless steels in order to meet DOE bipolar plate cost goals.

### **References**

1. K. Weisbrod, U.S. Patent 6,454,922 "Corrosion test cell for bipolar plates" September 24, 2002.

### **FY 2002 Publications/Presentations**

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**Special Recognitions & Awards/Patents Issued**